

CLAIMS

What is claimed is.

1. An electroplating composition comprising:
 2. copper;
 3. at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric, aminoacetic, fluoboric, and mixtures thereof;
 4. at least one halogen;
 5. at least one additive, selected from an accelerating agent, a suppressing agent, and an accelerating-suppressing agent; and
 6. the solution and mixture products thereof.
1. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of an accelerating agent and a suppressing agent.
1. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of an accelerating agent and an accelerating-suppressing agent.
1. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of a suppressing agent and an accelerating-suppressing agent.

1 5. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent is selected from a disulfide organic compound, a monosulfide organic
3 compound, and mixtures thereof.

1 6. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent is provided in a concentration range from about 2 micromole/liter to about 500
3 micromole/liter.

1 7. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent comprises 1-propane sulfonic acid, and 3,3'-dithio-bis di-sodium salt.

1 8. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent comprises 1-propane sulfonic acid, 3-[(ethoxy-thiomethyl)thio], - potassium
3 salt..

1 9. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent comprises (O-Ethyldithiocarbonato)-S-(3-sulfopropyl)-ester, potassium salt.

1 10. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent comprises a phosphonated disulfide.

1 11. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent is selected from a sulphonated monosulfide and a phosphonated monosulfide.

1 12. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating agent is selected from 3-mercaptopropanesulfonic acid and 2-
3 mercaptoethanesulfonic acid sodium salt.

1 13. The aqueous electroplating composition according to claim 1, wherein the
2 suppressing agent is provided in a concentration range from about 0.6 micromole/liter to about
3 600 micromole/liter.

1 14. The aqueous electroplating composition according to claim 1, wherein the
2 suppressing agent is selected from at least one of a polyether, polyethylene glycol, polypropylene
3 glycol, polyoxyethylene lauryl ether, polyethynene oxide, alkoxylated beta-naphtol, alkyl
4 naphthalene sulphonate, polyimines, poly amines, and polyamids.

1 15. The aqueous electroplating composition according to claim 1, wherein the
2 suppressing agent comprises a beta-naphtol having the structure:



5 wherein n may be equal to 1 and wherein m may be equal to 1, and wherein the
6 molecular weight is in the range from about 800 to about 1,500.

1 16. The aqueous electroplating composition according to claim 1, wherein the
2 suppressing agent comprises a cross-linked polyamide in a concentration range from about 0.6

3 μ mole/liter to about 600 μ mole/liter, and wherein the cross-linked polyamide has an average
4 molecular weight in a range from about 2,000 to about 3,000 gram/mole.

1 17. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating-suppressing agent is provided in a concentration range from about 1 μ mole/liter to
3 about 500 μ mole/liter.

1 18. The aqueous electroplating composition according to claim 1, wherein the
2 accelerating-suppressing agent comprises 1-propanesulfonic acid, 3-[[dimethylamino)-
3 thioxomethyl]- sodium salt..

1 19. A method of plating comprising:
2 providing aqueous electroplating composition, comprising:
3 copper;
4 at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric,
5 aminoacetic, fluoboric, and mixtures thereof;
6 at least one halogen ion;
7 at least one additive, selected from an accelerating agent, a suppressing
8 agent, and an suppressing-accelerating agent; and
9 the solution and mixture products thereof
10 contacting a substrate with the plating composition; and
11 impressing a multi-step direct-current waveform potential upon the substrate,
12 wherein the multi-step direct current waveform potential comprises a stepped changing
13 current density.

1 20. The method of plating according to claim 19, wherein impressing a multi-step
2 direct-current waveform potential upon the substrate further comprises:
3 applying a direct-current waveform potential upon the aqueous electroplating
4 composition before contacting the substrate therewith.

1 21. The method of plating according to claim 19, wherein the method further
2 comprises:
3 pre-treating the substrate with a composition selected from deionized water, distilled
4 water, an acid, a base, a solvent, a reducing agent, and mixtures thereof.

1 22. The method of plating according to claim 19, wherein the contacting the substrate
2 comprises rotating the substrate relative to the plating composition at a rate in a range from about
3 0 to about 500 rpm.

1 23. The method of plating according to claim 19, wherein contacting the substrate
2 comprises supplying plating composition at a rate from about 3 L/min to about 60 L/min.

1 24. The method of plating according to claim 19, wherein the plating composition is
2 maintained in a temperature range from about 7 C to about 35 C.

1 25. The method of plating according to claim 19, wherein the multi-step direct current
2 waveform potential comprises a stepped changing current density that comprises:
3 a nucleation current density; followed by
4 an initiation current density; followed by
5 at least one cycle of a fill current density that comprises a first forward pulse
6 current density and a second reverse pulse current density; and followed by
7 a bulk fill current density.

1 26. The method of plating according to claim 19, wherein the multi-step direct current
2 waveform potential comprises a stepped increasing current density that comprises:
3 a nucleation current density in a range from about 3 mA/cm² to about 70 mA/cm².

1 27. The method of plating according to claim 19, wherein the at least one cycle of a
2 fill current density that comprises a first forward pulse current density and a second reverse pulse
3 current density comprises cycles in the range from 1ns to about 1 min.

1 28. The method of plating according to claim 19, before contacting a substrate with
2 the plating composition, the method further comprising:
3 forming a seed layer comprising copper upon the substrate, wherein forming a
4 seed layer is selected from physical vapor deposition and chemical vapor deposition.

1 29. An article comprising:
2 a substrate containing a recess therein, wherein the recess has a characteristic
3 width in a range from about 0.02 microns to about 100 microns,; and
4 a copper conductor in the recess, wherein the copper conductor has a grain size in
5 a range from about 5 nm to about 100 nm.

1 30. The contact according to claim 29, wherein the recess has an aspect ratio in a
2 range from about 1:1 to about 10:1.

1 31. The contact according to claim 29, wherein the grain originates from a <111>
2 crystal configuration.

1 32. The contact according to claim 29, wherein the grain originates from a <200>
2 crystal configuration.